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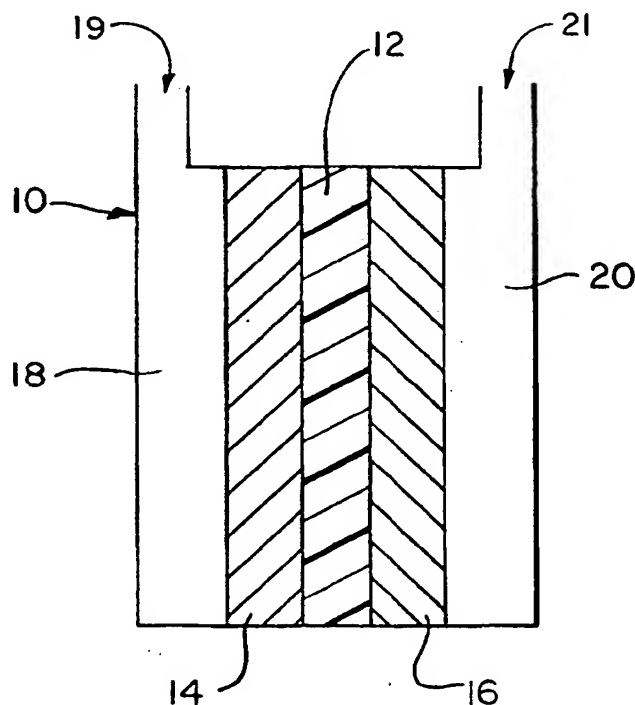
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(54) Title: SULFONATED POLYMERS FOR SOLID POLYMER ELECTROLYTES**(57) Abstract**

Sulfonated polyphenylene solid polymer electrolytes having high proton conductivity are provided, which are stable and which maintain high conductivity at temperatures of 100 °C and above. These membranes are useful as solid polymer electrolytes (12) in fuel cells (10) and can be operated above the boiling point of water.



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**SULFONATED POLYMERS
FOR SOLID POLYMER ELECTROLYTES**

Field of the Invention

This invention relates to stable sulfonated polyphenylene solid polymer electrolytes which have high proton conductivity characteristics. The sulfonated polyphenylene electrolytes are particularly useful in battery and fuel cell applications.

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Background of the Invention

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Solid polymer electrolytes, SPE's, are ionic polymers having very high ion conductivity. As electrolytes they are useful in electrochemical systems, primarily in batteries and fuel cells. The polymeric nature of SPE's makes them much easier to handle than liquid electrolytes. The physical construction of the electrochemical cell is greatly simplified with the use of SPE's since elaborate seals and containment systems are not needed to contain corrosive liquid electrolytes. The use of SPE's in fuel cells and batteries is well established in the art.

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The use of solid polymer electrolytes can greatly simplify cell design. Liquid electrolytes must be confined with a separator and contained with seals. Liquid electrolytes are highly corrosive and more readily contaminated than solid electrolytes. Fuel and oxygen will diffuse across liquid electrolytes more readily, lowering efficiency. SPE's avoid these problems and can be made thinner, thereby lowering cell resistance.

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1 Handling of SPE's is much easier than handling liquid
systems, and cell construction can be simpler.

Fuel cells with SPE's promise greater energy density
than liquid electrolyte cells because of low overall
5 weight, primarily due to simpler construction and thinner
cells. The first fuel cells flown in the U.S. space
program used sulfonated polystyrene SPE's, and SPE cells
are still a choice for space missions. (Alkaline cells
are also used.)

10 An SPE should have the following properties:
(1) high ionic conductivity, (2) zero electronic
conductivity, (3) very low permeability to gases,
(4) chemical stability at the operating temperature,
(5) mechanical strength, (6) low sensitivity to humidity,
15 and (7) compatibility with catalyst.

The first of these is by far the most difficult to
obtain. Current SPE's must be operated at temperatures
and pressures where water is a liquid; otherwise, the
membrane dehydrates, and proton conductivity is
20 drastically reduced. Although byproduct water must be
removed, care must be taken not to dry out the SPE. Water
management is a major difficulty of currently available
SPE's. Fuel and air streams must be pre-humidified, and
temperature strictly limited to avoid dehydration. These
25 extra control systems add significant weight and cost.

It would be highly advantageous to operate SPE fuel
cells above the boiling point of water. This would
greatly simplify water balance. Temperatures lower than
about 80°C require active cooling with concomitant weight
and cost. The key lies in development of an SPE with high
30 proton conductivity in the absence of condensed water.
The need for hydration with sulfonated polyfluorocarbon
SPE's is a result of the relatively low concentration of
sulfonate groups and the hydrophobic nature of the
35 fluorocarbon backbone. The structure of
perfluorosulfonated polymer membranes is such that the
sulfonate groups tend to concentrate in a water rich

1 phase, which forms a network permeating the hydrophobic
fluorocarbon regions. When dehydrated, the sulfonate
groups become isolated, and proton migration between
groups is difficult.

5 There is therefore a need for SPE's which maintain
high proton conductivity above the boiling point of water
and in the absence of liquid water.

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1 Summary of the Invention

 In accordance with practice of the present invention,
a solid polymer electrolyte is provided which comprises a
rigid-rod polyphenylene polymer which has been sulfonated
5 to contain from about 1% to about 30% by weight sulfur.

 Products incorporating the rigid-rod polyphenylene
polymer are also provided. In one embodiment, a fuel cell
is provided which includes an anode and a cathode, along
with means for introduction of fuel to the anode and means
10 for introduction of oxidant to the cathode. The
sulfonated polyphenylene polymer electrolyte of the
present invention provides electrolytic contact between
the anode and cathode.

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1 Brief Description of the Drawings

5 These and other features, aspects, and advantages of the present invention will be more fully understood when considered with respect to the following detailed description, appended claims, and accompanying drawings, wherein:

10 FIG. 1 is an elevation view of a sheet of film formed from a sulfonated rigid-rod polyphenylene polymer provided in accordance with practice of the present invention;

FIG. 2 is a schematic view, in partial cross-section, of a fuel cell incorporating a sulfonated rigid-rod polyphenylene polymer electrolyte provided in accordance with practice of the present invention;

15 FIG. 3 is a graph of sulfonation level in mol percent as a function of reaction time (hrs) at room temperature provided by the Example 2 experiment; and

20 FIG. 4 is a graph showing the conductivity of sulfonated polymers having two different degrees of sulfonation.

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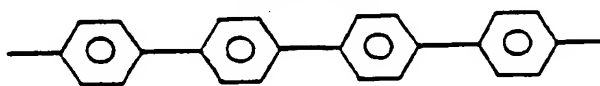
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1 Detailed Description of the Invention

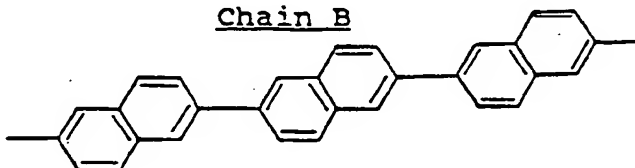
1 general structures shown here, for simplicity. All
structures shown represent polymers with various extents
of 1,4 linkages. Other linkages, including 1,2 phenylene
5 linkages, 1,3 phenylene linkages, and all the possible
naphthalene and anthracene linkages, are not shown, but
implied.

The rigid-rod polymers of the present invention are
linear polymers with parallel covalent bonds between the
monomer units. The monomer units are not necessarily in
10 a straight line. In some polymers, the majority of
monomer units will be in a straight line (see chain A
below). In other polymers, the monomer units will be
staggered in a stair-like or crankshaft-like fashion (see
chain B below). (The chain A and B monomer units are
15 shown schematically without pendant organic side groups.)
The monomer units can rotate about the linear axis of the
covalent bonds between the monomers. However, the monomer
units are restricted from flexing with respect to the
bond, thus forming a rigid-rod polymer. Although the
20 covalent bonds between the monomer units do not
necessarily line up in a straight line, i.e., they may not
be co-linear, the bonds are parallel, to yield a
substantially linear rigid-rod polymer.

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Chain A

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Chain B

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1 Each phenylene unit may be substituted with groups
R₁, R₂, R₃, and R₄ (collectively, R). Phenylene units may
have all R's equal to H; that is, no side groups other
than hydrogen. The number and type of R's are chosen to
5 retain solubility of the polymer and to adjust other
properties, such as reactivity to sulfonation.
Preferably, at least 50% of the phenylene monomer units
will have at least one non-hydrogen solubilizing side
group R. More preferably, at least 80% of the phenylene
10 monomer units will have a solubilizing side group.

 The solubilizing side groups R may be chosen from a
wide variety of functional groups, including but not
limited to alcohol, aldehyde, alkaryl, alkoxy, alkyl,
alkyl or aryl amide, alkyl ketone, alkyl sulfide,
15 alkylsulfonate, alkylsulfonic acid, amide, amine,
aralkyl, aryl, aryl ester, aryether,
aryletheretherketone, aryletherketone, arylketone,
aryloxy benzoyl, aryloxy, arylsulfide, arylsulfonate,
arylsulfone, arylsulfonic acid, arylsulfoxide, benzoyl,
20 carboxylic acid, ester, fluoro or polyfluoro alkyl,
fluoro or polyfluoro aryl, heteroaryl, imide, imine,
ketone, naphthyl, naphthoyl, phenoxybenzoyl, phenyl,
sulfonamide, sulfonate, sulfone, sulfonic acid, -CHOHAr,
-CHOHAr'-O-Ar, -CO₂Ar, -CO-Ar'-O-Ar, -OCOAr, and the
25 like, where -Ar is an aryl group and -Ar'- is an arylene
group. A given rigid-rod composition may have two or more
different R groups. The R groups may also be oligomeric
or polymeric, for example, but not limited to
poly(phenylene oxide), poly(ether ketone), poly(ether
30 ether ketone), poly(phenylene sulfide), poly(ethylene
oxide), and the like.

 Rigid-rod polyphenylene polymers and the production
thereof are disclosed in International Publication No.
WO91/02764, and in corresponding U.S. patent application
35 Serial No. 07/397,732, filed August 23, 1989 and allowed
December 23, 1992. Publication No. WO91/02764 and

1 application No. 07/397,732 are fully incorporated herein
by this reference.

5 The term "solubilizing group" means a functional
group which, when attached as a side chain to the polymer
in question, will render it soluble in an appropriate
solvent system. It is understood that various factors
must be considered in choosing a solubilizing group for a
particular polymer and solvent, and that, all else being
the same, a larger or higher molecular weight solubilizing
10 group will induce a higher degree of solubility.
Conversely, for smaller solubilizing groups, matching the
properties of the solvent and solubilizing groups is more
critical, and it may be more necessary to have, in
addition, other favorable interactions inherent in the
15 structure of the polymer to aid in solubilization.

One can estimate the compatibility of a solvent and
pendant organic substituent type by comparing properties,
such as dielectric constant and dipole moments. There are
also various types of semi-empirical sets of parameters
20 for non-polymeric materials (such as Hildebrand's
solubility parameters - J.H. Hildebrand and R.I. Scott,
The Solubility of Non-electrolytes, 3rd Ed., Dover
Publications, NY, 1964 - and derivatives thereof) that can
be used to estimate compatibility. Different sets of
25 these solubility parameters have been developed to account
for various types of solvent/solute interactions (e.g.,
dispersion interactions, induction, and dipole
interactions), and higher solubility is achieved as more
of these sets of parameters are matched. Other factors
30 being equal, a relatively higher molecular weight pendant
organic group will have a greater effect than a relatively
lower molecular weight group on the solubility
characteristics of the overall polymer. Therefore, it is
generally preferred that the solubilizing organic groups
35 be of moderately high molecular weight; that is, molecular
weight of greater than about 300. Furthermore, when the
molecular weight of the pendant organic groups is greater

1 than about 300, they can act as the functional equivalent
of the coil-like matrix of a molecular composite.
Solubility can be provided, however, with pendant groups
having very low molecular weight, such as phenyl groups,
5 phenyl ketone groups, hydroxy groups, and the like.

Processes for preparing unsubstituted or alkyl substituted polyphenylenes from aryl Grignard reagents are described in T. Yamamoto et al, Bull. Chem. Soc. Jpn., 1978, 51, 2091 and M. Rehahn et al, Polymer, 1989, 30, 1054. Paraphenylene polymers (made up of monomer units of Formula IA) can be prepared by the coupling of Grignard reagents with paraphenyl dihalides catalyzed by transition metal complexes. Thus, a mixture of 4-bromophenylmagnesium bromide (1 mole) and 4-bromo-3-alkylphenylmagnesium bromide (0.01 mole), the alkyl group
15 having an average chain length of about 24 carbon atoms, will react in an ether solvent in the presence of a transition metal complex to yield a polyparaphenylene rigid-rod polymer having about one monomer unit per 100 monomer units substituted with a long-chain alkyl group. The transition metal-catalyzed coupling reaction proceeds selectively and quantitatively under mild conditions. In another variant of the reaction, 1,4-dibromobenzene (1.0 mole) and a 1,4-dibromobenzene substituted with a long-chain alkoxy group (0.1 mole) can be coupled in the
25 presence of magnesium metal and a transition metal catalyst in an inert solvent, such as ether, to produce a polyparaphenylene rigid-rod polymer having, on the average, about one monomer unit out of 10 monomer units substituted with a long-chain alkoxy group. The net reaction resembles the dehalogenation polymerization of dihaloaromatic compounds with copper and sodium. Dibromosubstituted compounds are the compounds of choice for the reaction; however, in many instances, the dichloro
30 compound can also be used if the reaction can be initiated. We have found that the NiCl_2 (2,2'-bipyridine)
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1 transition metal catalyst works satisfactorily for this reaction.

Coupling of the paradihaloarene monomers is preferably carried out with nickel or palladium catalysts, with zinc as the reducing agent. Such polymerizations give soluble rigid-rod polyparaphenylene polymers with high molecular weights in virtually quantitative yields. This approach has distinct advantages, since a wider variety of solvents can be employed, such as N,N-dimethylformamide (DMF), N-methylpyrrolidinone (NMP), hexamethylphosphoric triamide (HMPA), and benzene. This coupling reaction can also be used with monomers having specially reactive groups, such as nitrile and carbonyl groups. In addition, zinc is less expensive and easier to handle than magnesium.

It is highly recommended to utilize highly purified (preferably greater than about 99% pure) paradihalobenzene monomer from which any water or other aprotic impurities have been removed. For instance, a mixture of one equivalent of anhydrous nickel chloride, three equivalents of sodium iodide, seven equivalents of triphenyl phosphine, and 50 equivalents of zinc metal is effective in the polymerization of about 30 equivalents of substituted paradichlorobenzene monomer. The polymerization reaction is preferably carried out at about 50°C but is effective from about 25°C to about 100°C. The ratio of equivalents of monomer to equivalents of nickel catalyst can vary over the range from about 10 to about 5000, and the ratio of equivalents of zinc to equivalents of monomer is at least 1.0. The ratio of equivalents of phosphine ligands and inorganic salt promoter to equivalents of nickel catalyst varies from about 1.0 to about 10 or more.

Aryl group coupling to afford polyphenylenes has also been effected by the palladium catalyzed condensation of haloaryl boronic acids as reported by Y. H. Kim et al, Polymer Preprints, 1988, 29, 310 and M. Rehahn et al,

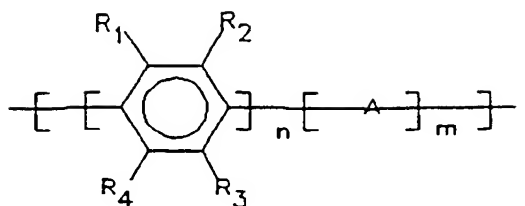
1 Polymer, 1989, 30, 1060. The para-haloaryl boronic acid
monomers required for formation of polyparaphenylenes can
be prepared by the monolithiation of the paradihalobenzene
5 with butyl lithium at low temperature and subsequent
trimethylborate quench and aqueous acid workup. These
polymerizations are carried out in aromatic and ethereal
solvents in the presence of a base such as sodium
carbonate. Therefore, this type of reaction is suitable
10 for producing polyparaphenylenes substituted with organic
groups such as alkyl, aryl, aralkyl, alkaryl,
polyfluoroalkyl, alkoxy, polyfluoroalkoxy, and the like.

The monomer units are known or can be prepared by
conventional chemical reactions from known starting
15 materials. For example, the paradihalobenzene monomers
substituted at the 2 position with an alkoxy group can be
prepared from the corresponding 2,5-dihalophenol by
allowing the phenol, in the presence of sodium hydroxide
and benzyltriethylammonium chloride, to react with the
20 corresponding 1-haloalkyl, such as 1-bromohexadecane.

In one embodiment of the present invention, the
rigid-rod polyphenylene is a co-polymer. In another
embodiment, it is a co-polymer of two or more rigid
25 phenylene monomer units. In another embodiment, it is a
co-polymer of at least one rigid phenylene monomer unit
and at least one flexible monomer unit. The co-polymers
may be random, block, graft, or other types known in the
art. Preferably, the rigid-rod segments will have number
30 average degree of polymerization of about 6 or greater.
The following structure is a block co-polymer where -A-
represents a flexible group, segment or block:

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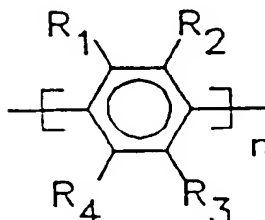


II

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wherein

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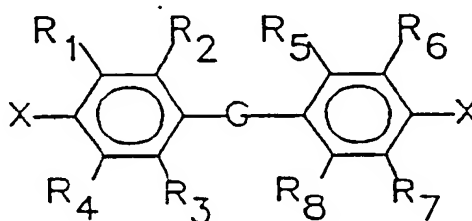


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is a rigid-rod polymer segment, wherein each R_1 , R_2 , R_3 , and R_4 on each monomer unit, independently, is H or a solubilizing side group, n and m are 1 or greater, and $-[A]-$ is a non-rigid segment, for example, as derived from non-rigid monomers of Structure III:

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III

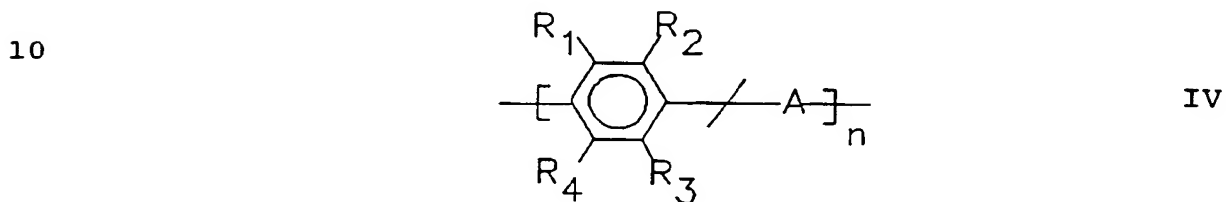
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where R_1 - R_8 are independently chosen from solubilizing side groups and H, wherein G is $-O-$, $-S-$, $-CH_2-$, $-CY_2-$, $-OCH_2-$, $-OAr-$, $-O(ArO)_n-$, $-(CH_2)_n-$, $-(CY_2)_n-$, $-CO-$, $-CO_2-$, $-CONY-$, $-O(CH_2CH_2O)_n-$, $-(CF_2)_n-$, $-COArCO-$, $-CO(CH_2)_nCO-$, $-C(CF_3)_2-$, $-C(CF_3)(Y)-$, $-NY-$, $-P(=O)Y-$, X is Cl, or Br, or I, and Ar is an aromatic group, heteroaromatic group, or substituted aromatic group, and Y is independently selected from the

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1 group consisting of H, F, CF₃, alkyl, aryl, heteroaryl, or
aralkyl group, and n is 1 or greater.

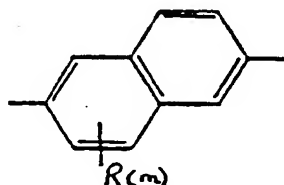
5 The following Structure IV shows a random co-polymer
provided in accordance with the present invention
comprising of a rigid-rod phenylene of Structure I and a
flexible monomer unit -A-:



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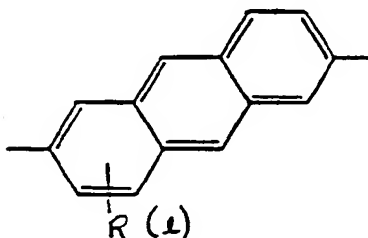
In another embodiment of the present invention the
rigid-rod polyphenylene will comprise rigid naphthalene or
anthracene monomer units, as follows:

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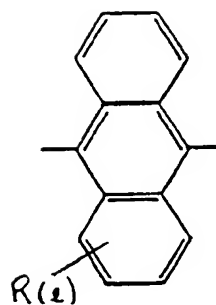
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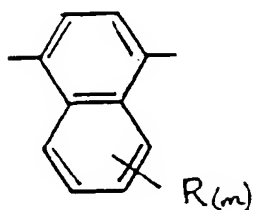
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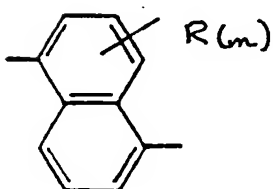
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VIII

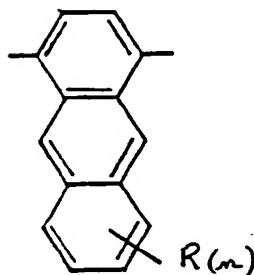
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IX

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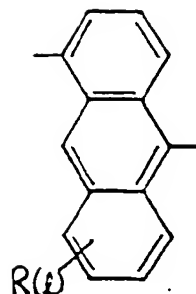


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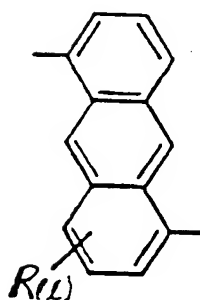
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XI

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XII

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wherein R_m and R_l are R groups as defined above, with $m = 1$ to 6 and $l = 1$ to 8.

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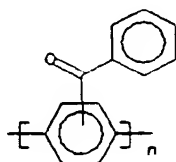
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Any position of the naphthalene or anthracene monomer units may bear solubilizing side groups. Non-rigid-rod monomer units may also be included, with preferably less than 20%, and more preferably less than 10% of the monomer units being non-rigid-rod units. Non-rigid-rod units are defined to include naphthalene units linked in the 1,3 or 1,6 or 2,7 positions, or anthracene units linked in the 1,3 or 2,7, or other non-parallel linkages of naphthalene or anthracene units. Flexible units, segments, blocks, or grafts -A- may also be included in the rigid-rod polyphenylenes having naphthalene or anthracene units.

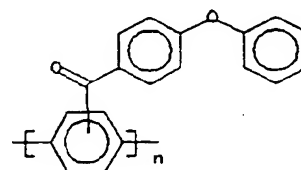
1 With the polymers of the present invention
incorporating phenylene units of the Structure I, if one
of the R's is benzoyl, with the other R's being hydrogen,
and most of the linkages are -1,4- phenylene linkages,
5 polymer 1 poly(benzoyl-1,4-phenylene) results. If one of
the R's is 4-phenoxybenzoyl, with the other R's being
hydrogen, the rigid-rod polyphenylene is poly(4-
phenoxybenzoyl-1,4-phenylene) 2.

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Note that the R groups benzoyl and 4-phenoxybenzoyl may be
randomly distributed between the 2 and 3 positions of the
phenylene units.

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Because of their unusual structure rigid-rod
polyphenylene polymers such as 1 and 2 have remarkable
physical properties. They are the stiffest and hardest of
all known isotropic thermoplastics. They have excellent
chemical and thermal stability. And they are processable
by both solution and thermal techniques.

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Ionic groups can be introduced into polyphenylenes by
sulfonation. Either the phenylene backbone or side groups
or both may be sulfonated. The aromatic rings of both
polymers 1 and 2 can be sulfonated using standard
techniques. Exemplary, but non-limiting sulfonation
methods include: treatment with concentrated sulfuric
acid, treatment with fuming sulfuric acid, treatment with
chlorosulfonic acid ClSO_3H followed by hydrolysis, or by
treatment with a mixture of sulfuric acid and thionyl
chloride. The time and temperature required will depend
on the particular side groups of the polyphenylene being

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1 sulfonated. In general, sulfonation conditions for a
 given rigid-rod polyphenylene can be determined as
 follows. The rigid-rod polyphenylene composition to be
 5 sulfonated (the test polymer) is first treated with
 concentrated sulfuric acid at room temperature for 16 hr
 and worked up as in Example 2 below. The resulting
 material is analyzed for sulfonic acid groups by
 titration. If the level of sulfonation is too low, the
 test sulfonation is repeated using more strenuous
 10 conditions roughly in the order:

	<u>Time</u>	<u>Temperature</u>	<u>Sulfonation Agent</u>
	24 hr	25°C	conc. sulfuric acid
	48 hr	25°C	"
	96 hr	25°C	"
15	200 hr	25°C	"
	24 hr	50°C	"
	24 hr	100°C	"
	48 hr	50°C	"
	24 hr	25°C	fuming sulfuric acid
	24 hr	50°C	"
	48 hr	50°C	"
20	24 hr	50°C	chlorosulfonic acid
	24 hr	100°C	"

The test sulfonation is repeated until the desired degree
 of sulfonation determined by titration is reached. In
 some cases sensitive side groups will not withstand
 25 sulfonation conditions and an alternate route involving
 protection of side groups or later incorporation of
 sensitive side groups will be necessary. Methods for
 protection and further elaboration of side groups will be
 apparent to those skilled in the art. The degree of
 30 sulfonation may be followed by other methods as
 convenient, including but not limited to elemental
 analysis, x-ray fluorescence, secondary electron or
 microprobe analysis.

If the initial test sulfonation conditions result in
 35 excessive sulfonation then the reaction temperature may be
 lowered or reaction time decreased to reach desired
 levels. In general, the mildest conditions which lead to

1 desired levels of sulfonation should be sought. For
example, sulfonation of the polymer 2 in sulfuric acid at
room temperature for 200 hr gives nearly the same level of
sulfonation obtained after reaction for 400 hours. The
5 phenoxy group of 2 polymer is relatively easily
sulfonated. Films and membranes prepared from sulfonated
polyphenylenes provided in accordance with the present
invention, such as the polymers 1 and 2, have high proton
conductivity.

10 The degree of sulfonation of the polyphenylene
polymers of the present invention is preferably at least
1% by weight, i.e., the weight of sulfur in the polymer
divided by the total weight of the polymer is at least 1%.
At levels less than 1%, the conductivity of the polymer is
15 less than desired. While there is no upper limit to the
preferable degree of sulfonation, it is not practical to
provide a polymer where the percent by weight sulfur is
greater than about 30%.

The degree of sulfonation may also be defined in
20 terms of mole percent by converting the above-described
weight percent to a mole percent value. For example, in
polymer 2, the molecular weight of the monomer unit is
272. Each sulfonic acid group adds a molecular weight of
80 to the monomer unit. If each monomer unit is
25 sulfonated once (on the average), the mole percent
sulfonated is 100%. The molecular weight of the
sulfonated monomer unit would be 352, and the percent
sulfur by weight is $32/352 = 9.1\%$. If each monomer unit
is sulfonated twice (on the average), the mole percent
30 sulfonation is 200%, and the percent sulfur by weight is
 $64/(272 + 2 \times 80) = 15\%$.

While not wishing to be bound by theory the high
conductivity of the rigid-rod SPE's results from the
linear array of sulfonic acid groups along the backbone.
35 Such arrangement facilitates transport of protons along
the chain. The rigidity of the polymer backbone also
prevents clustering of sulfonate groups and formation of

1 isolated regions of ionic groups which would prevent ion mobility.

5 Solid polymer electrolytes comprising sulfonated rigid-rod polyphenylene may be homopolymers, block co-polymers with rigid-rod blocks, random co-polymers, blends, alloys, mixtures, and the like. For the purposes of this invention rigid-rod polyphenylenes are taken to be polymers which incorporate sidechain substituted or unsubstituted rigid-rod polyphenylene blocks having number
10 average block length of about six or more, or blocks of naphthalene or anthracene monomer units having rigid-rod or crankshaft structures and number average block lengths of about six or more.

15 While SPE's are typically used in the form of a membrane other structures may be possible. For example, referring to FIG. 1, a sheet or film 10 of a sulfonated rigid-rod polyphenylene provided in accordance with the present invention is shown. Such a film can be provided by various film-forming techniques, including extrusion,
20 casting, and the like.

For fuel cell applications the SPE is typically in intimate physical contact with the electrodes, catalyst, current collector and other supporting structure. The SPE may not have readily distinguished physical boundaries.
25 It may be used as part of a gas diffusion electrode where gas, liquid and solid form a complex interface. The methods of construction of such electrodes and cells are well known in the art. For example, turning to FIG. 2, a schematic illustration of a fuel cell 11 incorporating a
30 solid polymer electrolyte comprising a sulfonated rigid-rod polyphenylene 12 provided in accordance with practice of the present invention is provided. The sulfonated polyphenylene separates and provides electrolytic contact between the anode 14 and the cathode 16. Fuel is
35 introduced into the compartment 18 via the inlet 19 for contact with the anode 14, while oxidant is introduced

1 into the compartment 20 via the inlet 21 for contact with
the cathode 16.

The sulfonated polyphenylenes of the present
invention will have other applications besides fuel cells.
5 For example, the SPE's of the present invention will be
useful as battery separators, electrolytes for
electrosynthesis cells, electrolytes for electrolysis
cells, electrolytes for gas generating electrochemical
systems, as ionic membranes in electrochemical sensors, as
10 electrolytes in electrochemical scrubbers and other
purification systems, and as electrolytes in primary and
secondary batteries. In some of these applications the
SPE will be used in a salt form, for example with sodium
counter ions or other alkali metal cation counter ions.
15 Other applications for the SPE's of the present invention
will be apparent to one skilled in the art.

It will be understood by one skilled in the art that
the exact composition of the SPE will depend on its
environment. The degree of hydration will depend on the
20 humidity and temperature. If the SPE is immersed in a
liquid the composition of the liquid will determine the
state of the SPE. The SPE may exchange protons, other
cations, and to some extent anions with the surrounding
solution. The pH of the SPE may be changed by adjusting
25 the pH of the liquid phase in contact with the SPE. The
SPE may be entirely in the acid form, meaning essentially
all of the sulfonic groups are protonated. The SPE may be
in the sodium form where all the sulfonic groups have
sodium cations as counter ions. Other cations may be used
30 such as cesium, potassium, lithium, calcium, magnesium,
quaternary amines, or combinations of these. Transition
metals and heavy metals may also be counter ions, for
example where the ionic membrane is used to separate
mixtures of metal salts.

35 It will also be apparent to one skilled in the art
that the ionic polymers comprising the SPE's of the
present invention may be crosslinked to various extents.

1 Crosslinking changes the solubility and mechanical
properties of the SPE. Lightly crosslinked materials will
swell greatly in compatible solvents; more highly
crosslinked polymers will swell less. Crosslink density
5 may be used to optimize the ionic conductivity by
controlling the amount of solvent absorption into the SPE
network. Crosslinks may be formed before, during, or
after sulfonation. Typically, a bifunctional reactive
compound is mixed and allowed to react with the ionic
10 polymer.

GENERAL PROCEDURES

1. 2,5-dichlorobenzoyl-containing Compounds

A wide variety of 2,5-dichlorobenzoyl-containing
compounds (e.g., 2,5-dichlorobenzophenones and 2,5-
15 dichlorobenzamides) can be readily prepared from 2,5-
dichlorobenzoylchloride. Pure 2,5-dichlorobenzoylchloride
is obtained by vacuum distillation of the mixture obtained
from the reaction of commercially available 2,5-
dichlorobenzoic acid with a slight excess of thionyl
20 chloride in refluxing toluene. 2,5-dichlorobenzophenones
(e.g., 2,5-dichlorobenzophenone, 2,5-dichloro-4'-
methylbenzophenone, 2,5-dichloro-4'-methoxybenzophenone,
and 2,5-dichloro-4'-phenoxybenzophenone) are prepared by
the Friedel-Crafts benzoylations of an excess of benzene
25 or substituted benzenes (e.g., toluene, anisole, or
diphenyl ether, respectively) with 2,5-
dichlorobenzoylchloride at 0-5°C using 2-3 mole
equivalents of aluminum chloride as a catalyst. The solid
products obtained upon quenching with water are purified
30 by recrystallization from toluene/hexanes. 2,5-
dichlorobenzoylmorpholine and 2,5-dichloro-
benzoylpiperidine are prepared from the reaction of 2,5-
dichlorobenzoylchloride and either morpholine or
piperidine, respectively, in toluene with pyridine added
35 to trap the hydrogen chloride that is evolved. After
washing away the pyridinium salt and any excess amine, the
product is crystallized from the toluene solution.

1 2. Activated Zinc Powder

Activated zinc powder is obtained after 2-3 washings of commercially available 325mesh zinc dust with 1 molar hydrogen chloride in diethyl ether (anhydrous) and drying
5 in vacuo or under inert atmosphere for several hours at about 100-120°C. The resulting powder should be sifted (e.g., a 150mesh sieve seems to be satisfactory), to remove the larger clumps that sometimes form, to assure high activity. This material should be used immediately
10 or stored under an inert atmosphere away from oxygen and moisture.

Example 1Preparation of Poly(Benzoyl-1,4-phenylene)

15 Anhydrous bis(triphenylphosphine) nickel(II) chloride (34.7g; 53mmole), triphenylphosphine (166.6g; 741mmole), sodium iodide (34.6g, 231mmole), and 325mesh activated zinc powder (181.8g, 2.8mole) are weighed into a bottle under an inert atmosphere and added to an oven dried 12-
20 liter flash containing 1.6 liters of anhydrous N-methylpyrrolidinone (NMP), against a vigorous nitrogen counterflow. This mixture is stirred for about 15 minutes, leading to a deep red coloration. Solid 2,5-dichlorobenzophenone and another 0.8 liters of anhydrous
25 NMP are then added to the flask. After an initial slight endotherm (due to dissolution of monomer), the temperature of the vigorously stirred reaction mixture warms to about 60°C over 30 minutes and is held there (60-65°C) by use of a cooling bath. After stirring for an additional 10-15
30 minutes, the viscosity of the reaction mixture increases drastically, and stirring is stopped. After heating this mixture for several days at 65°C, the resulting viscous solution is poured into 10L of 1 molar hydrochloric acid in ethanol to dissolve the excess zinc metal and to
35 precipitate the macromonomer. This suspension is filtered and the precipitate triturated with acetone and dried to afford 283g (85% yield) of a fine pale yellow powder.

1

Example 2Preparation of Poly(4-phenoxybenzoyl-1,4-phenylene)
2,5-Dichloro-4'-phenoxybenzophenone

5 To a 22L open-mouth round bottom flask fitted with a three-necked flange head, a mechanical stirrer, a nitrogen inlet and an outlet connected to a HCl scrubbing tower, is added 2,5-dichlorobenzoic chloride (4500g, 21.5mol) and phenyl ether (5489g, 32.3mol). The solution is cooled in ice to 5°C under stirring, and aluminum chloride (3700g, 10 27.8mol) is added slowly, over a period of about 10 minutes. The temperature of the reaction mixture is about 35°C after the addition. The mixture is then stirred for about 30 minutes and poured into about 20 gallons of ice water. The large reddish mass is dissolved by adding 15 about 12L of methylene chloride and stirring. The organic layer is separated and the aqueous layer is extracted with some methylene chloride. After methylene chloride is removed from the combined organic layer by distillation, the residue is recrystallized twice from cyclohexane 20 (2x10L), washed with cooled hexane, air dried, and then vacuum dried, to afford 5387g monomer (73%). The mother liquor is kept for later recovery of remaining product.

Poly(4-phenoxybenzoyl-1,4-phenylene)

25 To a 12L open-mouth round bottom flask equipped with a flange head, an air driven stirrer, a thermowell with a thermocouple, and a nitrogen purge line, is added under nitrogen bis(triphenylphosphine)nickel(II) chloride (58.2g, 88.9mmol), sodium iodide (54.7g, 365mmol), 30 triphenylphosphine (279.3g, 1065mmol), 325mesh activated zinc dust (239.5g, 3663mmol) and anhydrous N-methylpyrrolidinone (NMP) (3400ml). The solution is stirred and heated with a hot air gun to 40°C. The monomer 2,5-dichloro-4'-phenoxybenzophenone (935g, 35 2725mmol) is added. After about 15 minutes, the mixture becomes viscous. After 17 minutes, the solution becomes

1 very thick, and the stirring is stopped. The reaction
mixture is allowed to come to room temperature and is left
to stand overnight. The next morning, the reaction
mixture is coagulated into an acetone bath and ground up
5 in a blender. The crude polymer is then stirred for
several days in 1 molar hydrochloric acid in ethanol to
remove the excess zinc metal. The polymer is collected by
filtration, washed with water and acetone, and dissolved
in 16L of methylene chloride. The solution is filtered
10 through 10 μ m polypropylene membrane with the aid of
celite, coagulated in the same volume of acetone,
filtered, extracted with acetone for three days, and
dried, to afford 700g pale yellow polymer (94%).

15

Example 3

Sulfonation of Poly(4-phenoxybenzoyl-1,4-phenylene)

Twenty five grams of poly(4-phenoxybenzoyl-1,4-
phenylene), provided in accordance with a process such as
that outlined in Example 2, was dissolved in chloroform
and was reprecipitated by pouring into excess methanol.
20 This process was repeated three times. The resulting
solid was oven dried overnight at 100°C. The dry solid
was pulverized by hand in a mortar and pestle. Ten grams
of pulverized poly(4-phenoxybenzoyl-1,4-phenylene) was
25 dissolved in 100ml concentrated sulfuric acid under a
nitrogen atmosphere. The solution was held at room
temperature for the desired time (see figure) and then
poured into a large excess of water. The precipitate was
collected by filtration and washed with water. The
30 precipitate was pulverized and washed with water until the
wash water came to pH = 7. The sulfonated poly(4-
phenoxybenzoyl-1,4-phenylene) was then dialyzed against
distilled water using a cellulose acetate membrane.

35

The degree of sulfonation was determined by the
following procedure. One gram of sulfonated polymer was
placed in 1N aqueous sodium hydroxide, and the solution

1 was kept at room temperature for 1 day. The solution was
then back titrated with 1N HCl using phenolphthalein as an
indicator. FIG. 3 shows the level of sulfonation (mol%)
relative to the reaction time at room temperature.

5

Example 4

Preparation of SPE Membranes with Sulfonated Poly(4-phenoxybenzoyl-1,4-phenylene)

A sulfonated polymer prepared in accordance with the
10 procedure of Example 3 was dissolved in N-methyl-
pyrrolidinone (NMP) and reprecipitated into
tetrahydrofuran. The reprecipitated polymer was dried and
redissolved in NMP to make a 2% by weight solution.
Portions of this solution were cast onto clean glass
15 plates and dried under a nitrogen stream at 100°C for 10
hours. After drying, the membranes were removed from the
glass support to give films with thicknesses between 10
and 20 microns. These membranes were washed with methanol
to remove the last traces of NMP and dried at 100°C under
20 vacuum for 1 hour.

Example 5

Measurement of Proton Conductivity of Membranes of Sulfonated Poly(4-phenoxybenzoyl-1,4-phenylene)

25 Casting film samples (13mm in diameter, 10-20 μ m in
thickness) of sulfonated poly(4-phenoxybenzoyl-1,4-
phenylene) prepared in accordance with the procedure of
Example 4 were kept under the saturated vapor pressure of
water at room temperature in a desiccator for 1 week prior
30 to the measurements. The first sample had a 65.8 mol%
sulfonation, while the second sample was 80 mol%
sulfonated. The wet casting film samples were sandwiched
between platinum electrodes for electrical contacts and
packed in a sealed cell with stainless steel terminals
35 which were in contact with the measuring system.
Conductivity of the film was measured with a Yokokawa-
Hewlett-Packard Model 4192A LF impedance analyzer over the

1 frequency range 5 Hz to 13 MHz (OSC level 12 mV). The
complex impedance method was used to determine
conductivity.

5 The conductivity values as a function of temperature
for two samples having different degrees of sulfonation
are shown in FIG. 4. The conductivity peaks at about 0.02
S/cm at about 80°C. At 110°C the conductivity for both
samples is still above 4×10^{-3} S/cm.

10 The above descriptions of exemplary embodiments of
sulfonated polymers provided in accordance with the
present invention are for illustrative purposes. Because
of variations which will be apparent to those skilled in
the art, the present invention is not intended to be
15 limited to the particular embodiments described above.
The scope of the invention is described in the following
claims.

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1 WHAT IS CLAIMED IS:

1. A solid polymer electrolyte comprising a rigid-rod polyphenylene which has been sulfonated to contain from 1% to 30% by weight sulfur.

5

2. The solid polymer electrolyte of claim 1, wherein said rigid-rod polyphenylene has been sulfonated to 10% to 25% by weight sulfur.

10

3. The solid polymer electrolyte of claim 1, wherein the said sulfonated rigid-rod polyphenylene is part of a co-polymer.

15

4. The solid polymer electrolyte of claim 1, wherein the solubilizing groups R are selected from the groups consisting of -COAr, -CHOHAr, -OAr, -COAr'-O-Ar, alkaryl, alkyl, aralkyl, aryl, ester, and phenyl, where Ar is aryl and Ar' is arylene.

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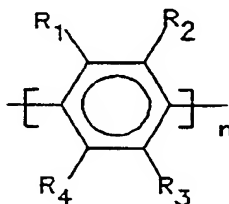
5. The solid polymer electrolyte of claim 1, wherein at least 80% of the phenylene units in the polyphenylene backbone are para or 1,4 linked.

25

6. The solid polymer electrolyte of claim 1, wherein at least 95% of the phenylene units in the polyphenylene backbone are para or 1,4 linked.

30

7. The solid polymer electrolyte of claim 1, wherein the said rigid-rod polyphenylene has the structure:



1 wherein $R_1 - R_4$ are solubilizing groups or $-H$, and n is 6
or greater, wherein the polymer has been sulfonated to
contain from 1% to 50% by weight sulfur.

5 8. The solid polymer electrolyte of claim 7,
wherein R_1 is phenoxybenzoyl, and $R_2 - R_4$ are H .

9. The solid polymer electrolyte of claim 7,
wherein R_1 is benzoyl, and $R_2 - R_4$ are H .

10

10. The solid polymer electrolyte of claim 7,
wherein $R_1 = R_2 = R_3 = R_4 = H$ on 0% to 20% of the phenylene units.

15 11. A fuel cell comprising an anode, a cathode,
means for introduction of fuel to the anode, means for
introduction of oxidant to the cathode, and a solid
polymer electrolyte of claim 1, providing electrolytic
contact between said anode and cathode.

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AMENDED CLAIMS

[received by the International Bureau on 17 May 1994 (17.05.94);
original claims 1-11 replaced by amended claims 1-11 (2 pages)]

1

1. An ion exchange structure comprising a solid polymer electrolyte comprising a rigid-rod polyphenylene which has been sulfonated to contain from 1% to 30% by weight sulfur.

5

2. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene has been sulfonated to 10% to 25% by weight sulfur.

10

3. The ion exchange structure of claim 1, wherein the sulfonated rigid-rod polyphenylene is part of a copolymer.

15

4. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene polymer includes solubilizing pendant groups R selected from the groups consisting of -COAr, -CHOHAr, -OAr, -COAr'-O-Ar, alkaryl, alkyl, aralkyl, aryl, and ester, where Ar is aryl and Ar' is arylene.

20

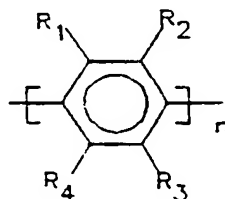
5. The ion exchange structure of claim 1, wherein at least 80% of the phenylene units in the polyphenylene backbone are 1,4 linked.

25

6. The ion exchange structure of claim 1, wherein at least 95% of the phenylene units in the polyphenylene backbone are 1,4 linked.

30

7. The ion exchange structure of claim 1, wherein the rigid-rod polyphenylene has the structure:



35

AMENDED SHEET (ARTICLE 19)

1 wherein $R_1 - R_4$ are solubilizing groups or $-H$, and n is
2 6 or greater.

3 8. The ion exchange structure of claim 7, wherein
4 R_1 is phenoxybenzoyl, and $R_2 - R_4$ are H .

5 9. The ion exchange structure of claim 7, wherein
6 R_1 is benzoyl, and $R_2 - R_4$ are H .

7 10. The ion exchange structure of claim 7, wherein
8 $R_1 = R_2 = R_3 = R_4 = H$ on 0% to 20% of the phenylene units.

9 11. A fuel cell comprising an anode, a cathode,
10 means for introduction of fuel to the anode, means for
11 introduction of oxidant to the cathode, and a solid
12 polymer electrolyte comprising a rigid-rod polyphenylene
13 which has been sulfonated to contain from 1% to 30% by
14 weight sulfur for providing electrolytic contact between
15 the anode and cathode.

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AMENDED SHEET (ARTICLE 19)

Fig. 1

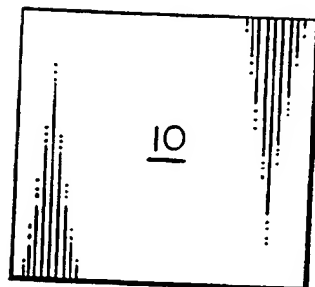
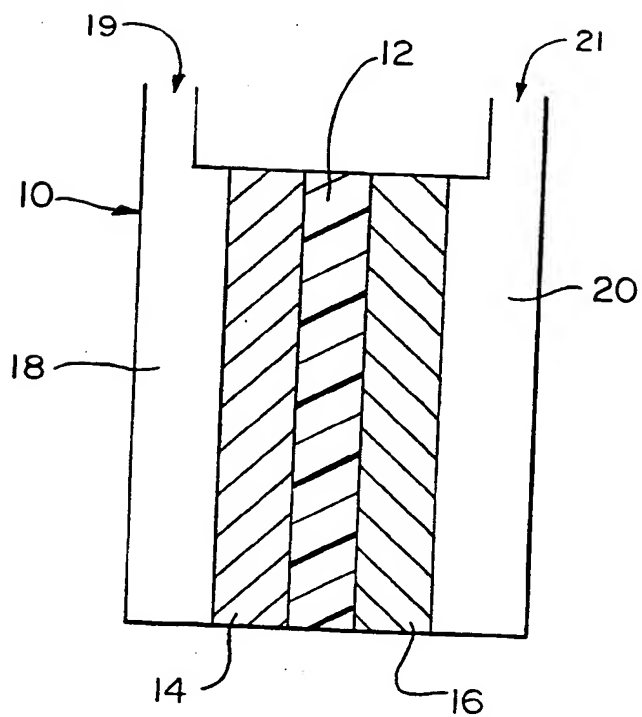
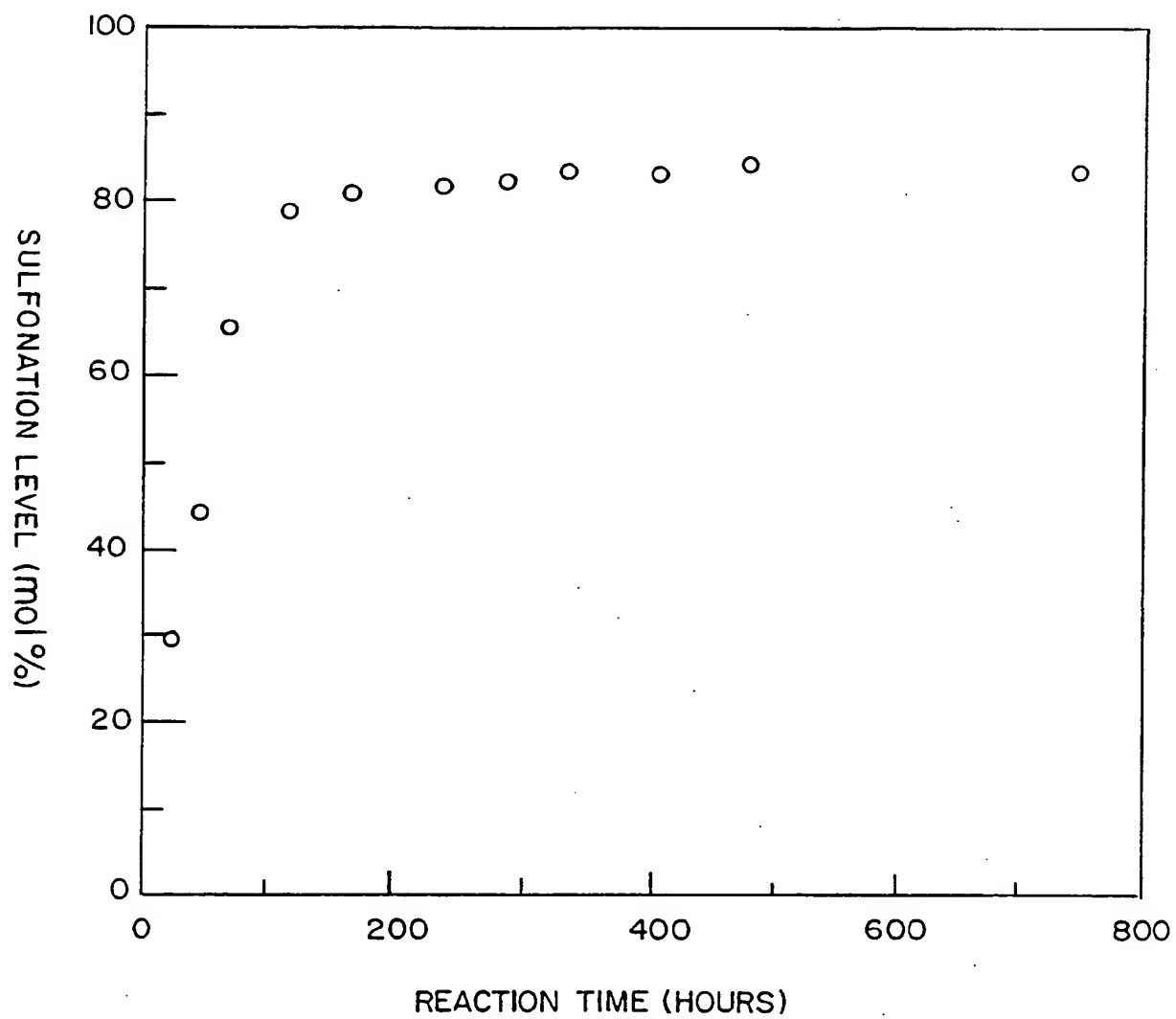


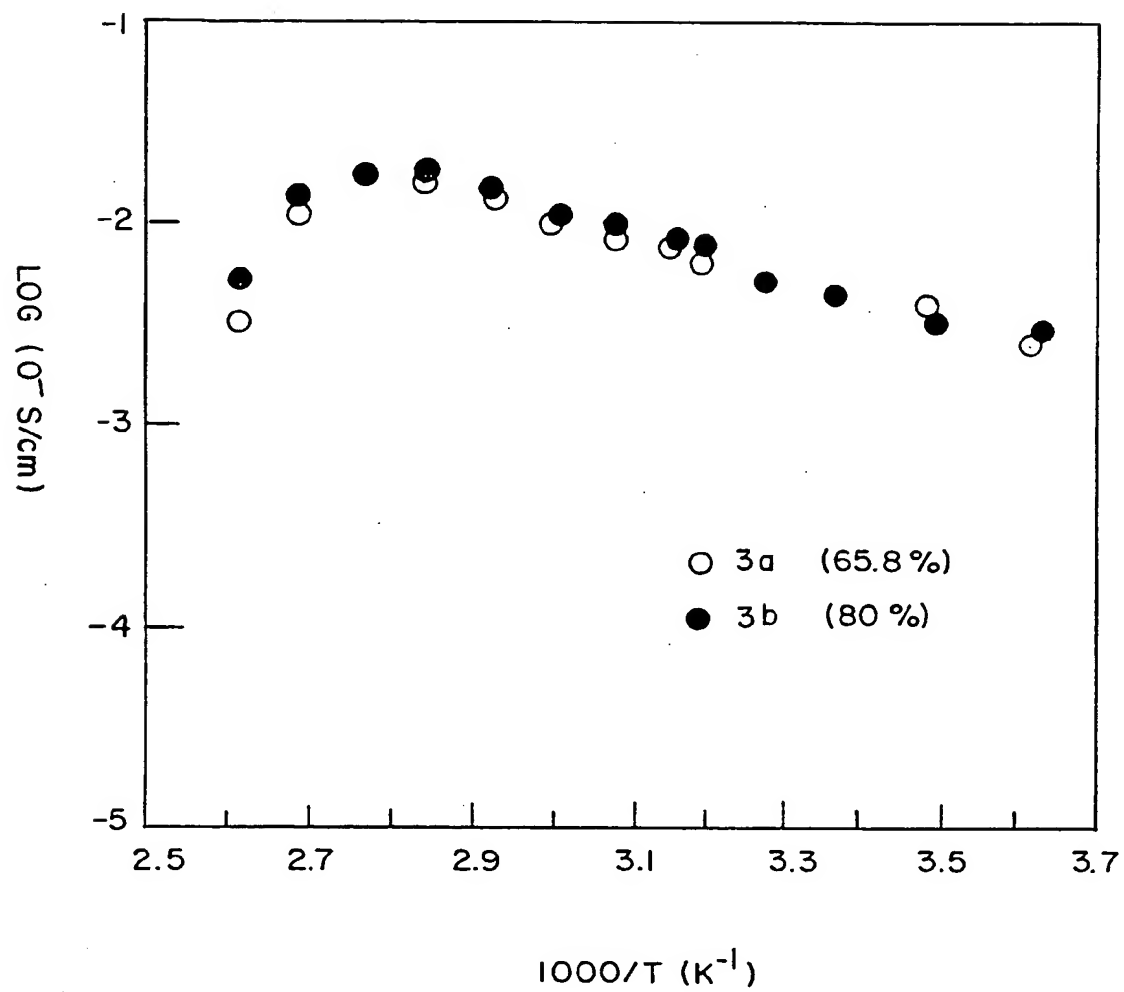
Fig. 2



2/3

Fig. 3

3/3

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

T/US94/01427

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01M 8/10

US CL :429/33

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/33, 192; 252/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US, A, 5,227,457 (Marrocco et al.) 13 July 1993, col. 9, lines 11-14 and 67.	1-10
X	US, A, 3,484,293 (Hodgdon) 16 December 1969, col. 3, lines 49-75.	1-7, 10, 11
A	US, A, 4,943,499 (Casalbore-Miceli et al.) 24 July 1990, col. 1, lines 36-60.	1-11
A	US, A, 3,651,030 (Desaulniers et al.) 21 March 1972, col. 2, lines 10-68.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

08 MARCH 1994

Date of mailing of the international search report

MAR 29 1994

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Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231Authorized officer

STEVE KALAFUT

Facsimile No. N.A.

Telephone No. (703) 308-0661

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